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London WC1R 5LX (GB)**(54) **High sulfur mineral oil compositions.**

(57) Copper corrosiveness of compositions comprising a major amount of a base oil of which at least 50% by volume is mineral oil that has an inherent sulfur content of at least 0.2 percent by weight is reduced by adding to the oil a small amount of at least one oil-soluble neutral hydrocarbyl phosphite ester, most preferably triphenyl phosphite. The addition of phosphite can yield composition exhibiting a copper rod rating of 5 or below in the Cincinnati Milacron Thermal Stability test procedure "A", even though in the absence of the addition of phosphite, the composition fails the test. The unpredictability of the invention is shown by the fact that not all high sulfur oils respond to the treatment, and no explanation for the divergence of results is presently known.

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This invention relates to reducing the copper corrosivity of mineral oils having a high content of natural or inherent sulfur components (i.e., sulfur components that are in the base oil as produced as distinguished from sulfur components which are deliberately introduced into oil as additives).

As is well known and documented in the literature, mineral oils produced or derived from certain petroleum crudes have relatively high inherent sulfur contents; e.g., 0.2 percent by weight and above. The chemical composition of such sulfur impurities is diverse and can involve complex molecular structures. For example, C. J. Thompson in a report entitled "Identification of Sulfur Compounds in Petroleum and Alternate Fossil Fuels" points out that a twenty year study of certain crude oils culminated in the identification of some 200 organic sulfur compounds present in the oil. In his report, which appears at pages 189-208 of "Organic Sulfur Chemistry", Invited Lectures Presented at the 9th International Symposium on Organic Sulfur Chemistry, Riga, USSR, 9-14 June 1980, Edited by R. Kh. Freidlina and A. E. Skorova, Pergamon Press, Copyright 1981, the author makes reference to certain other crude oils having sulfur contents as high as 13.9, 9.6 and 7.5 percent.

Unfortunately, when high sulfur refined or unrefined mineral oils (i.e., those containing 0.2% or more of sulfur in the form of inherent components) are used as lubricants or functional fluids in apparatus having so-called yellow metal parts (copper and copper alloys such as brass and bronze), the sulfur components tend strongly to corrode such copper-containing parts. A procedure widely used for assessing the severity of this corrosive attack is the copper rod corrosion test forming part of the Cincinnati Milacron Thermal Stability Test Procedure "A". See Cincinnati Milacron Lubricants Purchase Specification Approved Products Handbook, pages 3-1 to 3-3. A similar procedure has recently been issued by ASTM as ASTM D2270. This recent procedure is based on the foregoing Cincinnati Milacron procedure. The Cincinnati Milacron "A" test involves use of a rating scale which extends from 1 to 70. A rating of 5 or below is regarded as a pass, and the lower the numerical rating, the better. Conversely any rating above 5 is an unsatisfactory result and the higher the numerical rating above 5, the worse the result.

The discovery of an effective, low-cost way of reducing the corrosiveness of high sulfur mineral oils and mineral oil blends without eliminating or reducing the sulfur content of the oil would be a welcome contribution to the art. Such a contribution would conserve natural resources, reduce processing costs, and enhance performance and/or durability of engines and other mechanical apparatus utilizing high sulfur mineral oils as lubricants or functional fluids that are in contact, continuously or intermittently, with metal parts, especially readily-corroded metal parts such as those made of yellow metals.

This invention is deemed to constitute such a contribution.

This invention involves, inter alia, the discovery that it is possible to reduce the corrosiveness of high sulfur content mineral oils by use of small quantities of certain trivalent organic phosphorus additives, viz., oil-soluble neutral hydrocarbyl phosphites. By "neutral" is meant that the phosphite ester does not contain free unesterified acid functionality (i.e., it has no -OH or -SH groups). Moreover, it has been found that in at least some cases neutral hydrocarbyl phosphite esters can be used in extremely low concentrations in normally corrosive high sulfur oils, and yet provide a finished lubricant composition exhibiting very little corrosiveness toward copper.

Thus in one of its forms this invention provides an oil-based lubricant or functional fluid composition a major proportion of which is formed from a base mineral oil that has an inherent sulfur content of at least 0.2 percent by weight, said composition containing a minor amount of at least one oil-soluble neutral hydrocarbyl phosphite, said composition being characterized in that it exhibits a copper rod rating of 5 or below in the Cincinnati Milacron Thermal Stability test procedure in the form referred to in the specification hereof and in that in the absence of said phosphite, said composition exhibits a copper rod rating above 5 in said Cincinnati Milacron test procedure. In this embodiment an oil which fails the Cincinnati Milacron copper rod test is transformed by this invention into one that passes this test, preferably with a rating of 3 or below, more preferably with a rating of 2 or below, and most preferably with a rating of 1.

In another embodiment this invention provides a mineral oil composition characterized in that (i) the mineral base oil of the composition has an inherent sulfur content of 0.2% by weight or above, (ii) in the absence of a phosphite ester, said mineral base oil exhibits a copper rod rating below 5 in the Cincinnati Milacron Thermal Stability test, and (iii) the composition contains a corrosion-inhibiting amount of at least one oil-soluble neutral hydrocarbyl phosphite and exhibits a copper rod rating that is reduced by one or more numerical units of the rating scale as compared to the rating of said base oil in the absence of a phosphite ester. In this embodiment, a high sulfur oil which passes the Cincinnati Milacron copper rod test is transformed by this invention into one that exhibits even better corrosion resistance in the test, preferably with a rating of 3 or below, more preferably with a rating of 2 or below, and most preferably with a rating of 1.

While any oil-soluble sulfur-free neutral hydrocarbyl phosphite ester has the potential of decreasing the copper corrosivity of one or more mineral oils having an inherent sulfur content of 0.2% by weight or above, the use of oil-soluble, sulfur-free, neutral (i.e., fully esterified) hydrocarbyl monophosphites (i.e., one phosphorus atom per molecule) and/or diphosphites (i.e., two phosphorus atoms per molecule), and especially trihydrocarbyl phosphites is preferred. Thus use can be made of such compounds as trimethyl phosphite, triethyl phosphite, tripropyl phosphite, triisopropyl phosphite, tributyl phosphite, triisobutyl phosphite, triamyl phosphite, trihexyl phosphite, triheptyl phosphite, trioctyl phosphite, triisooctyl phosphite, tris(2-ethylhexyl) phosphite, trinonyl phosphite, tridecyl phosphite, triisodecyl phosphite, trilauryl phosphite, tris(tridecyl) phosphite, triallyl phosphite, trioleyl phosphite, tricyclohexyl phosphite, tribenzyl phosphite, tris(phenethyl) phosphite, phenyl dimethyl phosphite, phenyl diisodecyl phosphite, diphenyl isooctyl phosphite, diphenyl isodecyl phosphite, bis(2,4-di-tert-butylphenyl)pentaerythritol diphosphite, distearyl pentaerythritol diphosphite, phenyl neopentylene glycol phosphite, tetraphenyl dipropylene glycol diphosphite, tetra- C_{12-15} alkyl 4,4'-isopropylidenediphenol diphosphite, and diisodecyl pentaerythritol diphosphite. In general, each hydrocarbyl group may contain up to about 50 carbon atoms or more, provided only that the compound is sufficiently soluble in the oil to accomplish the corrosion inhibition objectives of this invention. Triaryl phosphites are generally the most effective for the purposes of this invention, and thus are preferred. Examples include cresyl diphenyl phosphite, tricresyl phosphite, trixylyl phosphite, tris(nonylphenyl) phosphite, trinaphthyl phosphite, and in general any oil-soluble triaryl phosphite in which each aryl group contains from 6 to 24 carbon atoms, more preferably 6 to 18 carbon atoms, and especially where the aryl hydrocarbyl group is phenyl or alkyl-substituted phenyl. Triphenyl phosphite is the most preferred additive because of its excellent performance characteristics, commercial availability, purity, and low cost.

The neutral phosphites are used in small amounts sufficient to decrease the copper corrosivity as assessed, for example, by the copper rod test of the Cincinnati Milacron test procedure. The amount used will thus vary depending upon the amount and character of the inherent sulfur components in the oil, the responsiveness of the oil to copper corrosion inhibition, the molecular weight of the neutral phosphite(s) being employed, and the extent to which it is desired to reduce the copper corrosiveness of the particular oil. Typically amounts of up to 0.05% by weight are sufficient but higher amounts can be used whenever deemed necessary or desirable. Preferably, the amount used falls in the range of 0.01 to 0.03 wt %.

Not all oils respond to use of neutral hydrocarbyl phosphite copper corrosion inhibitors pursuant to this invention. The reason for this is not known, but presumably relates in some way or other to the chemical structure(s) of the inherent sulfur component(s) present in the oil. Thus there is no presently-known way by which it can be predicted whether a given oil will or will not respond to use therein of a neutral hydrocarbyl phosphite copper corrosion inhibitor pursuant to this invention other than to conduct a pilot experiment with the particular high sulfur mineral oil. For this purpose, the Cincinnati Milacron copper rod test is used and indeed, is recommended for use, although other equivalent procedures may be found useful and can be used, if desired. Once a representative sample of a given high sulfur mineral oil has been found to respond to addition of one or more neutral hydrocarbyl phosphites, the remainder of such oil can be treated pursuant to this invention and thereby rendered resistant to copper corrosiveness.

The unpredictability of this invention is thus shown by the fact that not all high sulfur oils respond to the treatment, and no explanation for the divergence of results is presently known.

The compositions of this invention preferably contain, in addition to the hydrocarbyl phosphite ester(s), (a) one or more oil-soluble metal salts of one or more dihydrocarbyl phosphorodithioic acids, preferably one or more zinc dihydrocarbyl dithiophosphates; (b) one or more antioxidants, (c) one or more rust inhibitors, and/or (d) one or more demulsifiers. Compositions containing at least any two or any three of (a), (b), (c) and (d) are more preferred. Most preferably the compositions of this invention contain all of (a), (b), (c) and (d).

The oil-soluble metal salts of one or more dihydrocarbyl phosphorodithioic acids that can be employed in the compositions of this invention are salts in which the metal is a Group II metal, aluminum, tin, iron, cobalt, lead, molybdenum, manganese, nickel or copper. While various hydrocarbyl groups can be present in these salts, the hydrocarbyl groups are preferably primary or secondary alkyl groups (or a combination of primary and secondary alkyl groups), and most preferably are all primary alkyl groups. The preferred salts are the zinc salts, and although any oil-soluble zinc dihydrocarbyl dithiophosphate can be used as component (a), it is particularly preferred to employ an overbased zinc dihydrocarbyl dithiophosphate, especially a zinc dialkyl dithiophosphate wherein the alkyl groups are primary alkyl groups, containing from 6 to 10 carbon atoms each, especially 8 carbon atoms each, and wherein the overbased to neutral ratio is 0.96 or above as determined by ^{31}P nmr. In this connection, overbased species appear in the range of 103 to 105 ppm whereas neutral species appear in the range of 100 to 102 ppm and the signals are integrated in the usual manner to calculate the overbased : neutral ratio. Additionally the impurity content in the zinc

dihydrocarbyl dithiophosphate should be very low. Preferably at about 80 ppm, the ^{31}P nmr should provide an integrated spectrum showing less than about 0.25 area percent phosphorus. Also, it is preferable that at 5 to 15 ppm, the integrated ^{31}P nmr spectrum will show virtually no phosphate impurities. Likewise virtually no impurities should appear at 95 to 98 ppm in the integrated spectrum. It is also preferable to use zinc dihydrocarbyl dithiophosphates which exhibit a copper weight loss in the ASTM D2619 procedure of 0.70 maximum. Zinc di-(2-ethylhexyldithiophosphate) meeting the above criteria is especially preferred, particularly when employed in a formulation of other components such as in Example 3 hereinafter.

Other metal salts of dihydrocarbyl phosphorodithioic acids including other zinc dihydrocarbyl dithiophosphates which may be used in the compositions of this invention are referred to hereinafter.

While various oil-soluble antioxidants can be used, it is preferred to use a combination of (1) a hindered phenolic antioxidant such as a mixture of tertiary butyl phenols containing at least about 75% and preferably at least about 85% 2,6-di-tert-butylphenol, such as Ethyl® 735 antioxidant, and (2) a secondary aromatic amine antioxidant such as bis(4-alkylphenyl)amines wherein the alkyl groups contain from 6 to 12 carbon atoms and preferably are branched chain alkyl groups, such as Naugalube 438L antioxidant, a product in which the alkyl groups are branched octyl groups. The proportions of the phenolic antioxidant to the aromatic amine antioxidant are preferably in the range of about 3-14 parts by weight of the phenolic antioxidant per part by weight of the amine antioxidant. Preferred proportions are in the range of 5 to 10 parts by weight, and more preferably 6 to 8 parts by weight, of the phenolic antioxidant per part by weight of the amine. Other antioxidants suitable for use in the practice of this invention are referred to hereinafter.

All sorts of rust inhibitors can be employed in the compositions of this invention, and further reference to such materials appears hereinafter. However the preferred materials comprise a combination of (1) a modified imidazoline rust inhibitor, such as HITEC® 536 additive (Ethyl Petroleum Additives, Inc.; Ethyl Petroleum Additives, Ltd.; Ethyl S.A.; Ethyl Canada Limited); (2) one or more overbased alkaline earth metal alkyl phenates having a TBN (ASTM D2896) of over 200, most preferably a calcium alkyl phenate with a TBN of at least about 250, such as OLOA 219, Chevron Chemical Company; and (3) one or more alkaline earth dihydrocarbyl naphthalene sulfonates, most preferably a calcium dialkyl naphthalene sulfonate wherein the alkyl groups each contain 6 to 12 carbon atoms, most preferably 9 carbon atoms, such as NA-SUL® 729 inhibitor. The proportions of (1) : (2) : (3) are preferably in the ranges of 3-10 parts by weight of (1), and 2-7 parts by weight of (2) per part by weight of (3).

The demulsifier(s) used in the preferred compositions of this invention can likewise be varied. The preferred materials for the use are, however, liquid nonionic surface active agents, such as the amine glycol condensates such as are available under the TRITON trademark of Rohm & Haas Company. A particularly preferred material of this type is TRITON CF-32 which is described by the manufacturer as composed of 95% active component(s) and 5% water which is a pale yellow liquid having a Brookfield viscosity at 25°C of 550 cP, a specific gravity of 1.03 at 25°C, a density of 8.6 lb/gal, a pH (5% aqueous solution) of 9.5-11, a flash point (TOC) of < 300°F, and a pour point of 15°F (-9°C). Examples of other demulsifiers which can be used are referred to hereinafter.

The practice of this invention is illustrated by, but is not limited to, the following examples wherein all parts and percentages are by weight.

EXAMPLE 1

An additive concentrate is formed by blending together the following components: 53.33% zinc di-2-ethylhexyl dithiophosphate (Elco 108); 22.67% ETHYL® antioxidant 735 (a mixture of tertiary butyl phenols containing approximately 85% 2,6-di-tert-butyl phenol, 11% 2,4,6-tri-tert-butyl phenol, 2% 2,4-di-tert-butyl phenol, 2% other phenols); 4.67% 4,4'-bis(tert-nonyl)-1,1'-diphenylamine (Naugalube 438L); 1.33% overbased calcium sulfurized phenate (OLOA-219, a product indicated by the manufacturer, Chevron Chemical Company, to have a TBN (ASTM D2896) of 254, a calcium content of 9.25% and a sulfur content of 3.73%); 1.33% calcium dinonylnaphthalene sulfonate as a 50% solution in light mineral oil (NA-SUL® 729 additive); 6.67% modified imidazoline rust inhibitor (HITEC® 536 additive, a product indicated by the suppliers thereof, Ethyl Petroleum Additives, Inc., Ethyl Petroleum Additives, Ltd., Ethyl S.A., Ethyl Canada Limited, to have a neutralization number in the range of 51 to 61 mg KOH/g, typically 56; a typical specific gravity of 0.92 to 0.94; a typical viscosity at 100°C of 36 cSt); 0.4% amine polyglycol condensate nonionic surface active agent (TRITON® CF-32, a product indicated by the manufacturer, Rohm & Haas Company, to be a mixture of 95% active and 5% water having a Brookfield Viscosity @ 25°C of 550 cps; a specific gravity @ 25°C of 1.03; a pH of 9.5-11; a flash point (TOC) > 300°F and a pour point of 15°F (-9°C); 2.67% triphenyl phosphite; and 6.93% process oil diluent. The concentrate contains 0.2% calcium, 4.1% phosphorus, 4.2% zinc, and 8.1% sulfur, and has the following typical properties: viscosity at 40°C of 48.95

cSt, viscosity at 100 °C of 6.02 cSt, specific gravity (15.6/15.6 °C) of 0.995 and a flash point (P-M, °C) of 126). The concentrate can be employed in hydrocarbon based functional fluids such as hydraulic fluid at concentrations in the range of 0.50 to 1.25%, a preferred treat level being 0.75%.

5 EXAMPLE 2

An additive concentrate is formed by blending together the following components: 41.76% zinc di-2-ethylhexyl dithiophosphate (Elco 108); 18.94% ETHYL® antioxidant 735 (a mixture of tertiary butyl phenols containing approximately 85% 2,6-di-tert-butyl phenol, 11% 2,4,6-tri-tert-butyl phenol, 2% 2,4-di-tert-butyl phenol, 2% other phenols); 4.0% 4,4'-bis(tert-nonyl)-1,1'-diphenylamine (Naugalube 438L); 0.82% calcium dinonylnaphthalene sulfonate as a 50% solution in light mineral oil (NA-SUL® 729 additive); 10.0% modified imidazoline rust inhibitor (HiTEC® 536 additive, a product indicated by the suppliers thereof, Ethyl Petroleum Additives, Inc., Ethyl Petroleum Additives, Ltd., Ethyl S.A., Ethyl Canada Limited, to have a neutralization number in the range of 51 to 61 mg KOH/g, typically 56; a typical specific gravity of 0.92 to 0.94; a typical viscosity at 100 °C of 36 cSt); 6.47% sulfurized sperm oil replacement (SULPERM 10S, a product indicated by the manufacturer thereof, Keil Chemical Division of Ferro Corporation, to contain 9.5% sulfur and to have the following properties: a viscosity at 100 °F of 2000 SUS, a viscosity at 210 °F of 210 SUS, a specific gravity at 77 °F of 0.9844 and to exhibit an ASTM D130 rating of 1A); 0.35% poly-(oxyethylene)-poly(oxypropylene) derivative of ethylene diamine (a product marketed by BASF Corporation as TETRONIC 1501 and as PLURADYNE FL5151, and indicated to have the following typical properties: a molecular weight of 7900, a specific gravity (25 °/25 °C) of 1.02, a Brookfield Viscosity of 1170 cps at 25 °C, a pour point of -4 °C, and a refractive index at 25 °C of 1.4537); 2.35% triphenyl phosphite; and 15.29% process oil diluent. The concentrate can be employed in hydrocarbon based functional fluids, such as hydraulic fluid at concentrations in the range of 0.50 to 1.25%, a preferred treat level being 0.85%.

25 EXAMPLE 3

An additive concentrate is formed by blending together the following components: 42.67% zinc di-2-ethylhexyl dithiophosphate (HiTEC 678 additive, Ethyl Petroleum Additives, Inc., Ethyl Petroleum Additives, Ltd., Ethyl S.A., Ethyl Canada Limited); 28.33% ETHYL® antioxidant 735 (a mixture of tertiary butyl phenols containing approximately 85% 2,6-di-tert-butyl phenol, 11% 2,4,6-tri-tert-butyl phenol, 2% 2,4-di-tert-butyl phenol, 2% other phenols); 5.83% 4,4'-bis(tert-nonyl)-1,1'-diphenylamine (Naugalube 438L); 5.83% over-based calcium sulfurized phenate (OLOA 219, a product indicated by the manufacturer, Chevron Chemical Company, to have a TBN (ASTM D2896) of 254, a calcium content of 9.25% and a sulfur content of 3.73%); 8.33% modified imidazoline rust inhibitor (HiTEC® 536 additive, a product indicated by the suppliers thereof, Ethyl Petroleum Additives, Inc., Ethyl Petroleum Additives, Ltd., Ethyl S.A., Ethyl Canada Limited, to have a neutralization number in the range of 51 to 61 mg KOH/g, typically 56; a typical specific gravity of 0.92 to 0.94; a typical viscosity at 100 °C of 36 cSt); 0.5% amine polyglycol condensate nonionic surface active agent (TRITON® CF-32, a product indicated by the manufacturer, Rohm & Haas Company, to be a mixture of 95% active and 5% water having a Brookfield Viscosity @ 25 °C of 550 cps, a specific gravity @ 25 °C of 1.03, a pH of 9.5-11, a flash point (TOC) > 300 °F and a pour point of 15 °F (-9 °C); 0.25% poly(oxyethylene)-poly(oxypropylene) derivative of ethylene diamine (a product marketed by BASF Corporation as TETRONIC 1501 and as PLURADYNE FL5151, and indicated to have the following typical properties: a molecular weight of 7900, a specific gravity (25 °/25 °C) of 1.02, a Brookfield Viscosity of 1170 cps at 25 °C, a pour point of -4 °C, and a refractive index at 25 °C of 1.4537); 3.33% modified imidazoline corrosion inhibitor with a nitrogen content in the range of 5.5 to 5.8 and a boiling point of approximately 305 °F (MONAMULSE CI, a product supplied by Mona Industries and indicated by the supplier to have the following typical properties: a specific gravity @ 25 °C of approximately 0.959, an acid number in the range of 0-2, and an alkali number in the range of 100-120); 3.33% triphenyl phosphite; and 1.6% process oil diluent. The concentrate can be employed in hydrocarbon based functional fluids such as hydraulic fluid at concentrations in the range of 0.50 to 1.25%, a preferred treat level being 0.60%.

EXAMPLE 4

55 The procedure of Example 3 is repeated substituting 7.9% of trigecylphosphite for the triphenyl phosphite, and for best results increasing all treat levels referred to in Example 3 by an additional 0.03%.

EXAMPLE 5

The procedure of Example 3 is repeated substituting 10.8% of tributylphosphite for the triphenyl phosphite, and for best results increasing all treat levels referred to in Example 3 by an additional 0.05%.

EXAMPLE 6

The procedure of Example 3 is repeated substituting 20.5% of tris(2-ethylhexyl)phosphite for the triphenyl phosphite, and for best results increasing all treat levels referred to in Example 3 by an additional 0.13%.

EXAMPLE 7

An additive concentrate is formed by blending together the following components: 53.33% zinc di-2-ethylhexyl dithiophosphate (Elco 108); 19.0% ETHYL® antioxidant 735 (a mixture of tertiary butyl phenols containing approximately 85% 2,6-di-tert-butylphenol, 11% 2,4,6-tri-tert-butyl phenol, 2% 2,4-di-tert-butyl phenol, 2% other phenols); 4.00% 4,4'-bis(tert-nonyl)-1,1'-diphenylamine (Naugalube 438L); 0.8% calcium dinonylnaphthalene sulfonate as a 50% solution in light mineral oil (NA-SUL® 729 additive); 9.96% modified imidazoline rust inhibitor (HiTEC® 536 additive, a product indicated by the suppliers thereof, Ethyl Petroleum Additives, Inc., Ethyl Petroleum Additives, Ltd., Ethyl, S.A., Ethyl Canada Limited, to have a neutralization number in the range of 51 to 61 mg KOH/g, typically 56; a typical specific gravity of 0.92 to 0.94; and a typical viscosity at 100°C of 36 cSt); 0.39% amine polyglycol condensate nonionic surface active agent (TRITON® CF-32, a product indicated by the manufacturer, Rohm & Haas Company, to be a mixture of 95% active and 5% water having a Brookfield Viscosity @ 25°C of 550 cps, a specific gravity @ 25°C of 1.03, a pH of 9.5-11, a flash point (TOC) > 300°F and a pour point of 15°F (-9°C); 6.47% sulfurized sperm oil replacement (SUL-PERM 10S, a product indicated by the manufacturer thereof, Keil Chemical Division of Ferro Corporation, to contain 9.5% sulfur and to have the following properties: a viscosity at 100°F of 2000 SUS, a viscosity at 210°F of 210 SUS, specific gravity at 77°F of 0.9844 and to exhibit an ASTM D130 rating of 1A); 3.33% triphenyl phosphite; and 2.72% process oil diluent. The concentrate can be employed in hydrocarbon based functional fluids such as hydraulic fluid at concentrations in the range of 0.60 to 1.5%, a preferred treat level being 0.85%.

As noted above, the inclusion in the formulated high sulfur oils of a fully esterified monophosphite or diphosphite can reduce very substantially the copper corrosiveness of the resultant composition. For example, when a hydraulic oil of ISO viscosity grade 68 from a well known petroleum refiner with an inherent sulfur content of 0.43% was treated with an additive concentrate as described in Example 3 above such that the oil contained 0.02% by weight of the triphenyl phosphite, the Cincinnati Milacron copper rod ratings (triplicate runs) were in the range of 1-2. On the other hand, the same oil containing the same total concentration of a corresponding additive concentrate which did not contain any phosphite ester, the copper rod ratings (triplicate runs) were in the range of 6-7. Similarly, when the same hydraulic oil was treated with the additive concentrate of Example 4 above such that the content of tridecyl phosphite in the oil was 0.05%, the copper rod ratings in the triplicate runs were reduced from 6-7 to 2. The same oil with 0.07% of tributyl phosphite as the additive concentrate of Example 5 above brought the copper rod ratings down from 6-7 to 3. The same improvement was achieved in the same base oil with 0.15% of tris(2-ethylhexyl) phosphite as the additive concentrate of Example 6.

When the above high sulfur hydraulic oil was treated with the concentrate of Example 7 in amount such that the oil contained 0.02% of triphenyl phosphite, the copper rod ratings (run in triplicate) were in the range of 1-2 whereas the corresponding additive concentrate which did not contain phosphite ester yielded triplicate copper rod ratings in the range of 7-8 when tested in the same base oil.

When the additive concentrate of Example 1 was used in the above high sulfur hydraulic oil at a treat rate of 0.75 (whereby the triphenyl phosphite content of the oil was 0.02%), the following results were obtained in the Cincinnati Milacron Thermal Stability Test (average of 3 runs):

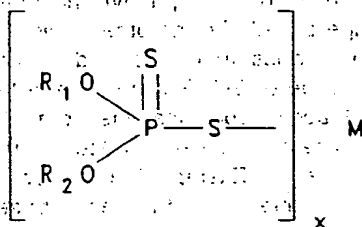
Property	Pass/Fail Point	Test Results
Copper Rod Rating	5 Maximum	1-2
Copper Weight Loss	10 mg/Maximum	1.1
Iron Appearance	1 Maximum	.1
Iron Weight Loss	10 mg Maximum	0.4
Total Sludge	100 mg Maximum	4.1

As also noted above, not all high sulfur oils respond favorably to the inclusion therein of a phosphite ester. For example in a mineral oil having an inherent sulfur content of 0.40% and an ISO viscosity grade 32 from a second well known petroleum refiner, 0.02% of triphenyl phosphite as the additive concentrate of Example 7 gave triplicate copper rod ratings in the range of 9-10. Yet in a mineral oil having an inherent sulfur content of 0.35 % and an ISO viscosity grade 68 from a third well known petroleum refiner, 0.02 % of triphenyl phosphite as the additive concentrate of Example 7 gave triplicate copper rod ratings in the range of 1-2, as compared to ratings in the range of 4-5 when the oil was treated with the corresponding phosphite-free additive concentrate.

As pointed out hereinabove, the compositions of this invention preferably contain one or more additional components, such as (a) one or more oil-soluble metal salts of one or more dihydrocarbyl phosphorodithioic acids, preferably one or more zinc dihydrocarbyl dithiophosphates, (b) one or more antioxidants, (c) one or more rust inhibitors, and/or (d) one or more demulsifiers.

(a) Metal Salts of Dihydrocarbyl Phosphorodithioic Acids

As is well known, metal hydrocarbyl dithiophosphates are usually prepared by reacting phosphorus pentasulfide with one or more alcohols or phenolic compounds or diols to produce a hydrocarbyl dithiophosphoric acid which is then neutralized with one or more metal-containing bases. When a monohydric alcohol or phenol is used in this reaction, the final product is a metal dihydrocarbyl dithiophosphate. On the other hand, when a suitable diol (e.g., 2,4-pentanediol) is used in this reaction, the final product is a metal salt of a cyclic hydrocarbyl dithiophosphoric acid. See, for example, U.S. Pat. No. 3,089,850. Thus typical oil-soluble metal hydrocarbyl dithiophosphates used as component a) may be represented by the formula



where R_1 and R_2 are, independently, hydrocarbyl groups or taken together are a single hydrocarbyl group forming a cyclic structure with the phosphorus and two oxygen atoms, preferably a hydrocarbyl-substituted trimethylene group of sufficient carbon content to render the compound oil soluble, M is a metal, and x is an integer corresponding to the valence of M . The preferred compounds are those in which R_1 and R_2 are separate hydrocarbyl groups (i.e., the metal dihydrocarbyl dithiophosphates). Usually the hydrocarbyl groups of the metal dihydrocarbyl dithiophosphates will contain no more than about 50 carbon atoms each although even higher molecular weight hydrocarbyl groups can be present in the compound. The hydrocarbyl groups include cyclic and acyclic groups, both saturated and unsaturated, such as alkyl, cycloalkyl, alkenyl, cycloalkenyl, aryl, cycloalkylalkyl, and aralkyl. It will be understood that the hydrocarbyl groups may contain elements other than carbon and hydrogen provided such other elements do not detract from the predominantly hydrocarbonaceous character of the hydrocarbyl group and do not adversely affect the copper corrosion resistance imparted to the composition pursuant to this invention. Thus the hydrocarbyl groups may contain ether oxygen atoms, secondary or tertiary amino nitrogen atoms, and/or inert

functional groups such as esterified carboxylic groups, and keto groups.

The metals present in the oil-soluble metal dihydrocarbyl dithiophosphates and oil-soluble metal cyclic hydrocarbyl dithiophosphates can include such metals as lithium, sodium, potassium, copper, magnesium, calcium, zinc, strontium, cadmium, barium, mercury, aluminum, tin, lead, chromium, molybdenum, tungsten, manganese, iron, cobalt, nickel, and ruthenium, as well as combinations of two or more such metals. Of the foregoing, the salts containing group II metals, aluminum, lead, tin, molybdenum, manganese, cobalt, nickel and/or copper, are preferred. The dihydrocarbyl dithiophosphates of zinc and copper are particularly preferred, with the zinc salts being the most preferred type of metal compound for use in the compositions of this invention.

The phosphorodithioic acids from which the metal salts are formed can be prepared by the reaction of about 4 moles of one or more alcohols (cyclic or acyclic) or one or more phenols or mixture of one or more alcohols and one or more phenols (or about 2 moles of one or more diols) per mole of phosphorus pentasulfide, and the reaction may be carried out within a temperature range of from 50 to 200°C. The reaction generally is completed in about 1 to 10 hours. Hydrogen sulfide is liberated during the reaction.

Another method for the preparation of the phosphorodithioic acids involves reaction of one or more alcohols and/or one or more phenols with phosphorus sesquisulfide in the presence of sulfur such as is described in PCT International Publication No. WO 90/07512. This reaction is conducted at an elevated temperature, preferably in the range of 85-150°C with an overall atomic P:S ratio of at least 2.5:1.

The alcohols used in forming the phosphorodithioic acids by either of the above methods are preferably primary alcohols, or secondary alcohols. Mixtures thereof are also suitable. The primary alcohols include propanol, butanol, isobutyl alcohol, pentanol, 2-ethyl-1-hexanol, isooctyl alcohol, nonanol, decanol, undecanol, dodecanol, tridecanol, tetradecanol, octadecanol, and eicosanol. The primary alcohols may contain various substituent groups such as halogen atoms and nitro groups, which do not interfere with the desired reaction. Among suitable secondary alcohols are included 2-butanol, 2-pentanol, 3-pentanol, 2-hexanol, and 5-methyl-2-hexanol. In some cases, it is preferable to utilize mixtures of various alcohols, such as mixtures of 2-propanol with one or more higher molecular weight primary alcohols, especially primary alcohols having from 4 to 13 carbon atoms in the molecule. Such mixtures preferably contain at least 10 mole percent of 2-propanol, and usually will contain from 20 to 90 mole percent of 2-propanol. In one preferred embodiment, the alcohol comprises about 30 to 50 mole percent of 2-propanol, about 30 to 50 mole percent isobutyl alcohol and about 10 to 30 mole percent of 2-ethyl-1-hexanol.

Other suitable mixtures of alcohols include 2-propanol/butanol, 2-propanol/2-butanol, 2-propanol/2-ethyl-1-hexanol, butanol/2-ethyl-1-hexanol, isobutyl alcohol/2-ethyl-1-hexanol, and 2-propanol/tridecanol.

Cycloaliphatic alcohols suitable for use in the production of the phosphorodithioic acids include cyclopentanol, cyclohexanol, methylcyclohexanol, cyclooctanol, and borneol. Preferably, such alcohols are used in combination with one or more primary alkanols such as butanol or isobutyl alcohol.

Illustrative phenols which can be employed in forming the phosphorodithioic acids include phenol, o-cresol, m-cresol, p-cresol, 4-ethylphenol, and 2,4-xyleneol. It is desirable to employ phenolic compounds in combination with primary alkanols such as propanol, butanol, hexanol, or the like.

Other alcohols which can be employed include benzyl alcohol, cyclohexenol, and their ring-alkylated analogs.

It will be appreciated that when mixtures of two or more alcohols and/or phenols are employed in forming the phosphorodithioic acid, the resultant product will normally comprise a mixture of three or more different dihydrocarbyl phosphorodithioic acids, usually in the form of a statistical distribution in relation to the number and proportions of alcohols and/or phenols used.

Illustrative diols which can be used in forming the phosphorodithioic acids include 2,4-pentanediol, 2,4-hexanediol, 3,5-heptanediol, 7-methyl-2,4-octanediol, neopentyl glycol, 2-butyl-1,3-propanediol, and 2,2-diethyl-1,3-propanediol.

The preparation of the metal salts of the dihydrocarbyl dithiophosphoric acids or the cyclic hydrocarbyl dithiophosphoric acids is usually effected by reacting the acid product with a suitable metal compound such as a metal carbonate, metal hydroxide, metal alkoxide, metal oxide, or other appropriate metal salt. Simply mixing and heating such reactants is normally sufficient to cause the reaction to occur and the resulting product is usually of sufficient purity for use in the practice of this invention. Typically, the salts are formed in the presence of a diluent such as an alcohol, water or a light mineral oil. Neutral salts are prepared by reacting one equivalent of metal oxide or hydroxide with one equivalent of the acid. Basic metal salts are prepared by adding an excess (i.e., more than one equivalent) of the metal oxide or hydroxide with one equivalent of the dihydrocarbyl phosphorodithioic acid or cyclic hydrocarbyl phosphorodithioic acid.

Illustrative metal compounds which may be used in such reactions include calcium oxide, calcium hydroxide, silver oxide, silver carbonate, magnesium oxide, magnesium hydroxide, magnesium carbonate,

magnesium ethoxide, zinc oxide, zinc hydroxide, strontium oxide, strontium hydroxide, cadmium oxide, cadmium hydroxide, cadmium carbonate, barium oxide, aluminum oxide, aluminum propoxide, iron carbonate, copper hydroxide, lead oxide, tin butoxide, cobalt oxide, nickel hydroxide, and manganese oxide.

In some cases, incorporation of certain ingredients such as small amounts of metal acetate or acetic acid in conjunction with the metal reactant will facilitate the reaction and provide an improved product. For example, use of up to about 5% of zinc acetate in combination with the required amount of zinc oxide tends to facilitate the formation of zinc dihydrocarbyl dithiophosphates.

Examples of useful metal salts of dihydrocarbyl dithiophosphoric acids, and methods for preparing such salts are found in the prior art such as for example, U.S. Pat. Nos. 4,263,150; 4,289,635; 4,308,154; 4,322,479; 4,417,990; 4,466,895; 4,904,401; 4,938,881; 4,941,984; 4,952,328; 4,957,649; and 4,981,602.

Generally speaking, the preferred types of metal salts of dihydrocarbyl dithiophosphoric acids are the oil-soluble metal salts of dialkyl dithiophosphoric acids. Such compounds generally contain alkyl groups having at least three carbon atoms, and preferably the alkyl groups contain up to 10 carbon atoms although as noted above, even higher molecular weight alkyl groups are entirely feasible. A few illustrative zinc dialkyl dithiophosphates include zinc diisopropyl dithiophosphate, zinc dibutyl dithiophosphate, zinc diisobutyl dithiophosphate, zinc di-sec-butyl dithiophosphate, the zinc dipentyl dithiophosphates, the zinc dihexyl dithiophosphates, the zinc diheptyl dithiophosphates, the zinc dioctyl dithiophosphates, the zinc dinonyl dithiophosphates, the zinc didecyl dithiophosphates, and the higher homologs thereof. Mixtures of two or more such metal compounds are often preferred for use such as metal salts of dithiophosphoric acids formed from mixtures of isopropyl alcohol and secondary butyl alcohol; isopropyl alcohol, isobutyl alcohol, and 2-ethylhexyl alcohol; isopropyl alcohol, butyl alcohol, and pentyl alcohol; and isobutyl alcohol and octyl alcohol.

As noted hereinabove, it is particularly preferred to employ an overbased zinc dihydrocarbyl dithiophosphate, especially a zinc dialkyl dithiophosphate wherein the alkyl groups are primary alkyl groups, containing from 6 to 10 carbon atoms each, especially 8 carbon atoms each, and wherein the overbased to neutral ratio is 0.96 or above as determined by ^{31}P nmr. In this connection, overbased species appear in the range of 103 to 105 ppm whereas neutral species appear in the range of 100 to 102 ppm and the signals are integrated in the usual manner to calculate the overbased to neutral ratio. Additionally, the impurity content in the zinc dihydrocarbyl dithiophosphate should be very low. Preferably at 80 ppm, the ^{31}P nmr should provide an integrated spectrum showing less than 0.25 area percent phosphorus, and at 5 to 15 ppm, the integrated ^{31}P nmr spectrum should show virtually no phosphate impurities. Likewise virtually no impurities should appear at 95 to 98 ppm in the integrated spectrum. It is also preferable to use zinc dihydrocarbyl dithiophosphates which exhibit a copper weight loss in the ASTM D2619 procedure of 0.70 maximum. Zinc di-(2-ethylhexyl)dithiophosphate meeting the above criteria is especially preferred.

(b) Antioxidants

The compositions of this invention preferably contain one or more antioxidants in order to protect the composition from premature degradation in the presence of air, especially at elevated temperatures. Typical antioxidants include hindered phenolic antioxidants, secondary aromatic amine antioxidants, oil-soluble copper compounds, and phosphorus-containing antioxidants.

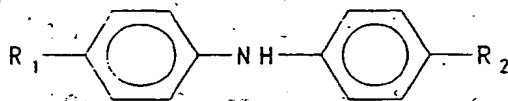
Illustrative sterically hindered phenolic antioxidants include ortho-alkylated phenolic compounds such as 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 2,4,6-tri-tert-butylphenol, 2-tert-butylphenol, 2,6-diisopropylphenol, 2-methyl-6-tert-butylphenol, 2,4-di-methyl-6-tert-butylphenol, 4-(N,N-dimethylaminomethyl)-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 2-methyl-6-styrylphenol, 2,6-di-styryl-4-nonylphenol, and their analogs and homologs. Mixtures of two or more such mononuclear phenolic compounds are also suitable.

Also useful in the compositions of this invention are methylene-bridged alkylphenols, and these can be used singly or in combinations with each other, or in combinations with sterically hindered unbridged phenolic compounds. Illustrative methylene bridged compounds include 4,4'-methylenebis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylenebis(2,6-di-tert-butylphenol), and similar compounds. Also useful are mixtures of methylene-bridged alkylphenols such as are described in U.S. Pat. No. 3,211,652.

Amine antioxidants, especially oil-soluble aromatic secondary amines can also be used in the compositions of this invention. Although aromatic secondary monoamines are preferred, aromatic secondary polyamines are also suitable. Illustrative aromatic secondary monoamines include diphenylamine, alkyl diphenylamines containing 1 or 2 alkyl substituents, each having up to about 16 carbon atoms, phenyl- α -naphthylamine, phenyl- β -naphthylamine, alkyl- or aralkyl-substituted phenyl- α -naphthylamine containing one

or two alkyl or aralkyl groups each having up to about 16 carbon atoms, alkyl- or aralkyl-substituted phenyl- β -naphthylamine containing one or two alkyl or aralkyl groups each having up to about 16 carbon atoms, and similar compounds.

A preferred type of aromatic amine antioxidant is an alkylated diphenylamine of the general formula



wherein R_1 is an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms) and R_2 is a hydrogen atom or an alkyl group (preferably a branched alkyl group) having 8 to 12 carbon atoms, (more preferably 8 or 9 carbon atoms). Most preferably, R_1 and R_2 are the same. One such preferred compound is available commercially as Naugalube 438L, a material which is understood to be predominately a 4,4'-dinonyldiphenylamine (i.e., bis(4-nonylphenyl)amine) wherein the nonyl groups are branched.

Another type of antioxidant that may be included in the compositions of this invention is comprised of one or more liquid, partially sulfurized phenolic compounds such as are prepared by reacting sulfur monochloride with a liquid mixture of phenols -- at least about 50 weight percent of which mixture of phenols is composed of one or more reactive, hindered phenols -- in proportions to provide from 0.3 to 0.7 gram atom of sulfur monochloride per mole of reactive, hindered phenol so as to produce a liquid product. Typical phenol mixtures useful in making such liquid product compositions include a mixture containing by weight about 75% of 2,6-di-tert-butylphenol, about 10% of 2-tert-butylphenol, about 13% of 2,4,6-tri-tert-butylphenol, and about 2% of 2,4-di-tert-butylphenol. The reaction is exothermic and thus is preferably kept within the range of 15°C to 70°C, most preferably between 40°C to 60°C.

If a sulfur-containing antioxidant is to be used, care should be taken to select one of composition and purity that does not denigrate the copper corrosion resistance imparted to the composition by the practice of this invention; and to use the antioxidant at a sufficiently low concentration to insure that such denigration does not occur.

Mixtures of different antioxidants can also be used. One suitable mixture is comprised of a combination of (i) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated monohydric phenols which is in the liquid state at 25°C; (ii) an oil-soluble mixture of at least three different sterically-hindered tertiary butylated methylene-bridged polyphenols; and (iii) at least one bis(4-alkylphenyl)amine wherein the alkyl group is a branched alkyl group having 8 to 12 carbon atoms; the proportions of (i), (ii) and (iii) on a weight basis falling in the range of 3.5 to 5.0 parts of component (i) and 0.9 to 1.2 parts of component (ii) per part by weight of component (iii).

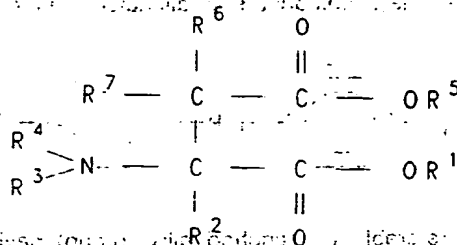
As noted above, it is preferred to use a combination of (1) a hindered phenolic antioxidant such as a mixture of tertiary butyl phenols containing at least about 75% and preferably at least about 85% 2,6-di-tert-butylphenol, such as Ethyl® 735 antioxidant, and (2) a secondary aromatic amine antioxidant such as alkylated diphenylamines wherein one and more preferably both of the phenyl groups are substituted by a branched alkyl group containing 6 to 12 and most preferably about 8 to 10 carbon atoms, such as Naugalube 438L.

(c) Rust Inhibitors

Various types of rust inhibitors are suitable for use in the compositions of this invention. These include dimer and trimer acids, such as are produced from tall oil fatty acids, oleic acid, or linoleic acid. Products of this type are currently available from various commercial sources, such as, for example, the dimer and trimer acids sold under the HYSTRENE trademark by the Humco Chemical Division of Witco Chemical Corporation and under the EMPOL trademark by Emery Chemicals. Another useful type of rust inhibitor for use in the practice of this invention are the alkenyl succinic acid and alkenyl succinic anhydride corrosion inhibitors such as, for example, tetrapropenylsuccinic acid, tetrapropenylsuccinic anhydride, tetradecenylsuccinic acid, tetradecenylsuccinic anhydride, hexadecenylsuccinic acid, and hexadecenylsuccinic anhydride. Also useful are the half esters of alkenyl succinic acids having 8 to 24 carbon atoms in the alkenyl group with alcohols such as the polyglycols. Other suitable corrosion inhibitors include ether amines, acid phosphates, amines, polyethoxylated compounds such as ethoxylated amines, ethoxylated phenols, and ethoxylated alcohols, and imidazolines. Materials of these types are well known to those skilled in the art.

and a number of such materials are available as articles of commerce.

Also useful as rust inhibitors are aminosuccinic acids or derivatives thereof represented by the formula:



wherein each of R^1 , R^2 , R^5 , R^6 and R^7 is, independently, a hydrogen atom or a hydrocarbyl group containing 1 to 30 carbon atoms, and wherein each of R^3 and R^4 is, independently, a hydrogen atom, a hydrocarbyl group containing 1 to 30 carbon atoms, or an acyl group containing from 1 to 30 carbon atoms. The groups R^1 , R^2 , R^3 , R^4 , R^5 , R^6 and R^7 , when in the form of hydrocarbyl groups, can be, for example, alkyl, cycloalkyl or aromatic containing groups. Preferably R^1 and R^5 are the same or different straight-chain or branched-chain hydrocarbon radicals containing 1-20 carbon atoms. Most preferably, R^1 and R^5 are saturated hydrocarbon radicals containing 3-6 carbon atoms. R^2 , either R^3 or R^4 , R^6 and R^7 , when in the form of hydrocarbyl groups, are preferably the same or different straight-chain or branched-chain saturated hydrocarbon radicals. Preferably a dialkyl ester of an aminosuccinic acid is used in which R^1 and R^5 are the same or different alkyl groups containing 3-6 carbon atoms, R^2 is a hydrogen atom, and either R^3 or R^4 is an alkyl group containing 15-20 carbon atoms or an acyl group which is derived from a saturated or unsaturated carboxylic acid containing 2-10 carbon atoms.

Most preferred of the aminosuccinic acid derivatives is a dialkylester of an aminosuccinic acid of the above formula wherein R^1 and R^5 are isobutyl, R^2 is a hydrogen atom, R^3 is octadecyl and/or octadecenyl and R^4 is 3-carboxy-1-oxo-2-propenyl. In such ester R^6 and R^7 are most preferably hydrogen atoms.

(d) Demulsifiers

Typical additives which may be employed as demulsifiers include alkyl benzene sulphonates, polyethylene oxides, polypropylene oxides, block copolymers of ethylene oxide and propylene oxide, and salts and esters or oil soluble acids.

Thus, for example use can be made of oxyalkylated trimethylol alkanes with molecular weights in the range of 1,000 to 10,000, and preferably in the range of 3,000 to 8,000. Preferably, the oxyalkylated trimethylol alkane is an oxyalkylated trimethylol ethane or propane, especially where the oxyalkylene groups are composed of a mixture of propyleneoxy and ethyleneoxy groups and where these groups are so disposed as to form relatively hydrophobic blocks adjacent the trimethylol group and relatively hydrophilic blocks remote the trimethylol group. Typical oxyalkylated trimethylol propane demulsifiers are described in U.S. Pat. No. 3,101,374. Commercially available products of this type are available from BASF Corporation under the Pluradot trademark. They are available in various molecular weights. Pluradot HA-510 has an average molecular weight of 4,600 and Pluradot HA-530 has an average molecular weight of about 5,300. Pluradot additives are propoxylated and ethoxylated trimethylol propanes.

Another type of suitable demulsifiers are oxyalkylated alkyl phenol-formaldehyde condensation products. Typically, these products have molecular weights in the range of 4,000 to 6,000 and are comprised of lower alkyl substituted phenol moieties joined together by methylene groups and in which the hydroxyl groups of the phenolic moieties have been ethoxylated. One such commercial product is marketed by Ceca S.A. of Paris, France under the "Prochinqr GR77" trade name. The product is supplied as a concentrate in an aromatic solvent and the active ingredient is believed to be an ethoxylated nonylphenol-formaldehyde condensate of molecular weight 4,200 (by gel permeation chromatography calibrated with polystyrene).

Another suitable type of demulsifier is comprised of the tetra-polyoxyalkylene derivatives of ethylene diamine, especially the tetra poly(oxyethylene)-poly(oxypropylene) derivatives of ethylene diamine. Materials of this type are available commercially from BASF Corporation under the "Tetronics" trademark. Materials of this general type are described in U.S. Pat. No. 2,979,528.

Mixtures of alkylaryl sulphonates, polyoxyalkylene glycols and oxyalkylated alkylphenolic resins, such as are available commercially from Petrolite Corporation under the TOLAD trademark, are also suitable. One

such proprietary product, identified as TOLAD 286K, is understood to be a mixture of these components dissolved in a solvent composed of alkyl benzenes. TOLAD 286 is believed to be a similar product wherein the solvent is composed of a mixture of heavy aromatic naphtha and isopropyl alcohol.

Preferred demulsifiers are proprietary materials available from BASF Corporation under the Pluronic trademark. These are block copolymers of propylene oxide and ethylene oxide.

Base Oils.

This invention is applicable to base oils containing at least 50%, preferably at least 70%, more preferably at least 80%, still more preferably at least 90%, and most preferably 100% by volume of mineral oil that has an inherent sulfur content of at least 0.2% by weight. Thus this invention can be applied to base oils or base oil blends composed entirely of mineral oils having this high inherent sulfur content. Alternatively, this invention can be applied to blends in which at least 50% of the blend is composed of mineral oil (which may itself be a blend of two or more mineral oils) having such high inherent sulfur content and the balance is composed of one or more synthetic or natural oils of lubrication viscosity.

The mineral oils not only can be hydrocarbon oils of lubricating viscosity derived from petroleum, but can be derived from tar sands, coal, and shale.

Suitable mineral oils include those of appropriate viscosity refined from crude oil of any source including Gulf Coast, Midcontinent, Pennsylvania, California, Alaska, Mexico, South America, Africa, Middle East, and the North Sea. Standard refinery operations may be used in processing the mineral oil. Among the general types of petroleum oils useful in the compositions of this invention are solvent neutrals, bright stocks, cylinder stocks, residual oils, hydrocracked base stocks, paraffin oils including pale oils, and solvent extracted naphthenic oils. Such oils and blends of them are produced by a number of conventional techniques which are widely known by those skilled in the art.

The base oil may be composed of a blend of one or more mineral oils with a high inherent sulfur content and one or more mineral oils with a low inherent sulfur content (if any), provided the resultant blend has a sulfur content of at least 0.2% by weight.

As is noted above, the base oil can be a blend which includes up to 50% by volume of one or more synthetic oils and/or one or more natural oils.

The synthetic oils comprise a variety of materials such as hydrogenated polyolefin oils; poly- α -olefins (e.g., hydrogenated or unhydrogenated α -olefin oligomers such as hydrogenated poly-1-decene); alkyl esters of dicarboxylic acids; complex esters of dicarboxylic acid, polyglycol and alcohol; alkyl esters of carbonic or phosphoric acids; polysilicones; fluorohydrocarbon oils; homo- and interpolymers of C_2 - C_{12} olefins; polyethers; polyglycols; silicates; alkylated aromatics; carbonates; thiocarbonates; orthoformates; borates; and halogenated hydrocarbons; among others.

Representative of such oils are homo- and interpolymers of C_2 - C_{12} monoolfinic hydrocarbons, alkylated benzenes (e.g., dodecyl benzenes, didodecyl benzenes, tetradecyl benzenes, dinonyl benzenes, di-(2-ethylhexyl)benzenes, wax-alkylated naphthalenes); and polyphenyls (e.g., biphenyls and terphenyls).

Alkylene oxide polymers and interpolymers and derivatives thereof where the terminal hydroxyl groups have been modified by esterification or etherification, constitute another class of synthetic oils which may be included in the blends with the high sulfur mineral oils. The alkylene oxide derived oils include those prepared through polymerization of alkylene oxides such as ethylene oxide or propylene oxide, and the alkyl and aryl ethers of these polyoxyalkylene polymers (e.g., methyl polyisopropylene glycol ether having an average molecular weight of 1,000, diphenyl ether of polyethylene glycol having a molecular weight of 500-1,000, diethyl ether of polypropylene glycol having a molecular weight of 1,000-1,500) or mono- and poly-carboxylic esters thereof, for example, the acetic acid ester, mixed C_3 - C_6 fatty acid esters, or the C_{13} Oxo acid diester of tetraethylene glycol.

Another type of synthetic oils which may be used with the high sulfur mineral oils comprises the esters of dicarboxylic acids (e.g., phthalic acid, succinic acid, maleic acid, azelaic acid, suberic acid, sebacic acid, fumaric acid, adipic acid, linoleic acid dimer) with a variety of alcohols (e.g., butyl alcohol, hexyl alcohol, dodecyl alcohol, 2-ethylhexyl alcohol, ethylene glycol). Specific examples of these esters include dibutyl adipate, di(2-ethylhexyl) adipate, didodecyl adipate, di(tridecyl) adipate, di(2-ethylhexyl) sebacate, di(2-ethylhexyl) sebacate, di-n-hexyl fumarate, dioctyl sebacate, diisooctyl azelate, diisodecyl azelate, dioctyl phthalate, didecyl phthalate, di(eicosyl) sebacate, the 2-ethylhexyl diester of linoleic acid dimer, and the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethylhexanoic acid.

Esters which may be used as synthetic oils also include those made from C_3 - C_{18} monocarboxylic acids and polyols and polyol ethers such as neopentyl glycol, trimethylolpropan, pentaerythritol and dipen-

taerythritol, Trimethylol propane tripelargonate and pentaerythritol tetracaproate, the ester formed from trimethylolpropane, caprylic acid and sebacic acid, and the polyesters derived from a C_3 - C_{14} dicarboxylic acid and on or more aliphatic dihydric C_3 - C_{12} alcohols such as derived from azelaic acid or sebacic acid and 2,2,4-trimethyl-1,6-hexanediol serve as examples.

Silicon-based oils such as the polyalkyl-, polyaryl-, polyalkoxy-, or polyaryloxysiloxane oils and silicate oils comprise another class of synthetic lubricants (e.g., tetraethyl silicate, tetraisopropyl silicate, tetra-(2-ethylhexyl) silicate, tetra(p-tert-butylphenyl) silicate, poly(methyl)siloxanes, and poly(methylphenyl)siloxanes. Other synthetic lubricating oils include liquid phosphate esters, e.g., tricresyl phosphate and trioctyl phosphate.

Also useful as base oil components are hydrogenated or unhydrogenated liquid oligomers of C_6 - C_{16} alpha-olefins, such as hydrogenated or unhydrogenated oligomers formed from 1-decene. Methods for the production of such liquid oligomeric 1-alkene hydrocarbons are known and reported in the literature. See for example U.S. Pat. Nos. 3,749,560; 3,763,244; 3,780,128; 4,172,855; 4,218,330; 4,902,846; 4,906,798; 4,910,355; 4,911,758; 4,935,570; 4,950,822; 4,956,513; and 4,981,578. Additionally, hydrogenated 1-alkene oligomers of this type are available as articles of commerce, for example, under the trade designations ETHYLFLO 162, ETHYLFLO 164, ETHYLFLO 166, ETHYLFLO 168, ETHYLFLO 170, ETHYLFLO 174, and ETHYLFLO 180 poly- α -olefin oils (Ethyl Corporation; Ethyl Canada Ltd.; Ethyl S.A.). Blends of such materials can also be used in order to adjust the viscometrics of the given base oil. Suitable 1-alkene oligomers are also available from other suppliers. As is well known, hydrogenated oligomers of this type contain little, if any, residual ethylenic unsaturation.

Preferred oligomers are formed by use of a Friedel-Crafts catalyst (especially boron trifluoride promoted with water or a C_{1-20} alkanol) followed by catalytic hydrogenation of the oligomer so formed using procedures such as are described in the foregoing U.S. patents.

Other catalyst systems which can be used to form oligomers of 1-alkene hydrocarbons, which, on hydrogenation, provide suitable oleaginous liquids include Ziegler catalysts such as ethyl aluminum sesquichloride with titanium tetrachloride, aluminum alkyl catalysts, chromium oxide catalysts on silica or alumina supports and a system in which a boron trifluoride catalyzed oligomerization is followed by treatment with an organic peroxide.

Typical natural oils that may be used as components of the base oils include castor oil, olive oil, peanut oil, rapeseed oil, corn oil, sesame oil, cottonseed oil, soybean oil, sunflower oil, safflower oil, hemp oil, linseed oil, tung oil, oiticica oil and jojoba oil. Such oils may be partially or fully hydrogenated, if desired, provided of course that they retain the desired physical properties.

Thus mixtures of high sulfur mineral oils with natural and/or synthetic oils can be used provided at least 50% by volume of the mixture is mineral oil with an inherent sulfur content of at least 0.2% by weight. The term "base oil" for this disclosure includes all the foregoing. In all cases, the base oils are only those which, when a neutral phosphite ester is included therein in accordance with this invention, yield a composition which achieves in the Cincinnati Milacron Thermal Test procedure, the copper rod rating improvements referred to hereinabove and in the claims hereof.

The lubricating oil compositions of this invention can thus be used in a variety of applications such as automotive crankcase lubricating oils, automatic transmission fluids, gear oils, hydraulic oils, or cutting oils. The preferred application is as power transmission fluids, especially hydraulic oils.

The fact that the base oils used in the compositions of this invention may be composed of (i) one or more high sulfur mineral oils, (ii) a blend of one or more low sulfur mineral oils with one or more high sulfur mineral oils, (iii) a blend of (i) with one or more synthetic oils, (iv) a blend of (ii) with one or more synthetic oils, (v) a blend of (i) with one or more natural oils, (vi) a blend of (ii) with one or more natural oils, (vii) a blend of (i) with one or more synthetic oils and one or more natural oils or (viii) a blend of (ii) with one or more synthetic oils and one or more natural oils does not mean that these various types of oils are necessarily equivalents of each other. Certain types of base oils may be used in certain compositions for the specific properties they possess such as high temperature stability, good low temperature viscometric properties, and inertness toward elastomers. In other compositions, other types of base oils may be preferred for reasons of availability or low cost. Thus, the skilled artisan will recognize that while the various types of base oils discussed above may be used in the compositions of this invention, they are not necessarily functional equivalents of each other in every instance.

In general, the additives are employed in the base oils in minor amounts sufficient to improve the performance characteristics and properties of the base oil or fluid. The amounts will thus vary in accordance with such factors as the viscosity characteristics of the base oil or fluid employed, the viscosity characteristics desired in the finished product, the service conditions for which the finished product is intended, and the performance characteristics desired in the finished product. However, generally speaking, the following

concentrations (weight percent) of the components (active ingredients) in the base oils or fluids are illustrative:

	General Range	Preferred Range	More Preferred Range	Particularly Preferred Range
Component a)	0.1 - 5	0.2 - 2	0.3 - 1.4	0.35 - 0.8
Component b)	0.01 - 2	0.1 - 1.5	0.15 - 1.2	0.2 - 1
Component c)	0 - 2	0.01 - 1.5	0.04 - 1.2	0.05 - 1
Component d)	0 - 2	0.001 - 1.5	0.005 - 1.0	0.01 - 0.5

The additive concentrates of this invention will usually contain up to 90 per cent by weight and preferably from 5 to 70 per cent by weight of one or more inert liquid diluents such as light mineral oil, with the balance being active ingredients such as those referred to hereinabove.

Claims

1. An oil-based lubricant or functional fluid composition which comprises a major proportion of at least one base oil of lubrication viscosity, at least 50% by volume of said base oil being a mineral oil that has an inherent sulfur content of at least 0.2 percent by weight, said composition having added thereto a minor amount of at least one oil-soluble neutral hydrocarbyl phosphite, said composition being characterized in that it exhibits a copper rod rating of 5 or below in the Cincinnati Milacron Thermal Stability test procedure "A" in the form referred to in the specification hereof and in that in the absence of the addition of said phosphite, said composition exhibits a copper rod rating above 5 in said Cincinnati Milacron test procedure.
2. A composition according to Claim 1 wherein at least 90% by volume of said base oil is mineral oil that has an inherent sulfur content of at least 0.2 percent by weight.
3. A composition according to Claim 1 wherein substantially all of said base oil is mineral oil that has an inherent sulfur content of at least 0.2 percent by weight.
4. A composition according to Claim 1 wherein said at least one oil-soluble neutral hydrocarbyl phosphite is at least one oil-soluble trihydrocarbyl phosphite.
5. A composition according to Claim 1 wherein said at least one oil-soluble neutral hydrocarbyl phosphite is at least one oil-soluble triaryl phosphite.
6. A composition according to Claim 1 wherein said at least oil-soluble neutral hydrocarbyl phosphite is triphenyl phosphite.
7. A composition according to Claim 1 wherein said composition to which said phosphite has been added exhibits a copper rod rating of 3 or below in said Cincinnati Milacron test procedure.
8. A composition according to Claim 1 wherein said composition to which said phosphite has been added exhibits a copper rod rating of 2 or below in said Cincinnati Milacron test procedure.
9. An oil-based lubricant or functional fluid composition which comprises a major proportion of at least one base oil of lubrication viscosity, at least 50% by volume of said base oil being a mineral oil that has an inherent sulfur content of at least 0.2 percent by weight, said composition having added thereto a minor amount of at least one oil-soluble neutral hydrocarbyl phosphite, said composition characterized in that (i) without the addition of said neutral phosphite ester, said composition exhibits a copper rod rating below 5 in the Cincinnati Milacron Thermal Stability test "A", and (ii) with the addition of said at least one oil-soluble neutral hydrocarbyl phosphite, said composition exhibits a copper rod rating that is reduced by one or more numerical units of the rating scale as compared to the rating of said base oil in the absence of the addition of said phosphite ester.
10. A method of reducing the copper corrosiveness of a composition which comprises a major proportion of at least one base oil of lubrication viscosity, at least 50% by volume of said base oil being a mineral

oil that has an inherent sulfur content of at least 0.2 percent by weight, said method comprising formulating said composition by adding thereto a minor copper-corrosion inhibiting amount of at least one oil-soluble neutral hydrocarbyl phosphite such that either (a) with the addition of said phosphite said composition exhibits a copper rod rating of 5 or below in the Cincinnati Milacron Thermal Stability test procedure "A" in the form referred to in the specification hereof, whereas in the absence of the addition of said phosphite, said composition exhibits a copper rod rating above 5 in said Cincinnati Milacron test procedure, or (b) in the absence of the addition of said phosphite, said composition exhibits a copper rod rating below 5 in said Cincinnati Milacron test procedure whereas with the addition of said phosphite, said composition exhibits a copper rod rating that is numerically smaller by at least one unit of the rating scale of said Cincinnati Milacron test procedure.

It is to be understood that the present invention is not limited to the specific details of the apparatus and methods described herein, and that various modifications and changes may be made without departing from the spirit and scope of the invention as defined by the appended claims.

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The following examples are given to illustrate the invention, but are not to be construed as limiting the scope of the invention. In the following examples, the weight of the oil was 100 grams, and the weight of the phosphite was 0.1 gram. The oil used was a mineral oil having an inherent sulfur content of 0.2 percent by weight. The phosphite used was a neutral hydrocarbyl phosphite having a molecular weight of 150. The oil and phosphite were mixed in a glass bottle, and the mixture was allowed to stand for 24 hours before being tested. The results of the tests are given in the following table.

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TABLE I

Oil Sulfur Content (wt %)	Phosphite (wt %)	Copper Rod Rating
0.2	0.1	5
0.2	0.0	6
0.2	0.2	4
0.2	0.3	3
0.2	0.4	2
0.2	0.5	1

It is to be understood that the present invention is not limited to the specific details of the apparatus and methods described herein, and that various modifications and changes may be made without departing from the spirit and scope of the invention as defined by the appended claims.

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(54) **High sulfur mineral oil compositions.**

(57) Copper corrosiveness of compositions comprising a major amount of a base oil of which at least 50% by volume is mineral oil that has an inherent sulfur content of at least 0.2 percent by weight is reduced by adding to the oil a small amount of at least one oil-soluble neutral hydrocarbyl phosphite ester, most preferably triphenyl phosphite. The addition of phosphite can yield composition exhibiting a copper rod rating of 5 or below in the Cincinnati Milacron Thermal Stability test procedure "A", even though in the absence of the addition of phosphite, the composition fails the test. The unpredictability of the invention is shown by the fact that not all high sulfur oils respond to the treatment, and no explanation for the divergence of results is presently known.

EP 0 552 863 A3



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EUROPEAN SEARCH REPORT

Application Number

EP 93 30 0041 -6

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. CL.5)
A	US-A-2 178 610 (P.L. SALZBERG) * page 3; example 4 *	1,4,5,9,10	C10M137/02 C10M141/10 C10M167/00 C10M169/04
A	US-A-2 058 344 (R.C. MORAN) * column 1, line 10 - line 15 * * column 2, line 15 - line 50 * * claim 1 *	1,4,5,9,10	/(C10M169/04,101:02,137:02) (C10N30:12) (C10N40:08)
A	GB-A-2 052 505 (THE LUBRIZOL CORPORATION) * page 1, line 22 - line 27 * * page 2, line 30 - line 31 * * page 5; table II *	1,4-6,9,10	
A	GB-A-1 262 378 (SHELL INTERNATIONAL RESEARCH MAATSCHAPPIJ) * page 2, line 31 - line 37 * * page 2, line 52 - line 55 * * page 3, line 41 - line 44 * * page 3, line 51 - line 54 *	1-5,9	
A	US-A-2 285 855 (F. B. DOWNING) * page 4, left column; line 73 - right column, line 5 * * claim 25 *	1,4-6,9,10	C10M
A	US-A-2 260 305 (E.F. ENGELKE) * page 1, right column; example 1 * * page 2, right column, line 33 - line 45 *		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 21 JUNE 1993	Examiner HILGENGA-K.J.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons * : member of the same patent family, corresponding document	

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